THE STUDY OF CHEMICAL COMPOSITION ON THE VEGETATION INSTALLED ON TAILINGS

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ABSTRACT
This paper is a study on identifying the amount of heavy metals extracted from the sterile, by the main species of spontaneuse plants, determined as prevailing on the waste dumps from Moldova Noua. Dominance of plant species ponds was determined using the method developed by Braun-Blanquet (1964) and followed for two years. The method of atomic absorption spectrophotometry at different wavelengths each chemical element was determined in part extracted from samples of dried herbs. The results confirmed that species *Salsola kali*, *Festuca arundinaceea*, *Medicago falcata* and *Phragmites australis* are the most tolerant plants to heavy metals, long resisted the sterile. Also, *Festuca arundinaceea* proved plant hiperacumulatoare the lead, *Medicago falcata* and sterile extract a large number of heavy metals, including manganese, zinc, iron, cadmium, copper and lead in significant amounts.
Keywords: vegetation, tailings, heavy metals

INTRODUCTION

The mining activity from the region of Moldova Noua, in the Caras- Severin county, led to the appearance of profound changes of the relief from this area, transformations of pedological, agrochemical and biological nature. (ROGOBETE and all., 1999). The sterile dumps resulted are an example of the anthropic impact on the area they are located. Their presence in the area determined especially the loss of biodiversity and they simplified the ecosystem structure. At Moldova Noua an area of about 306 hectares is occupied by these ponds/lakes of sterile tailings/dumps, considered to be the largest in Romania. Due to the studies on the composition of the heavy metals of this sterile tailing (coming from the Tausani lake) there were significantly higher results concerning the zinc and nikel content.(MICU, 2011). Following the research on the existence of a spontaneous vegetation on sterile tailings from Moldova Noua, there were identified 41 species of plants arranged uniformly on the surface of three tailing ponds: Tăuşani, Boşneag 1 şi Boşneag 2. (MICU, 2011). The general appearance of the vegetation on the ponds was that of two groups of individuals more or less monospecific herbaceous plant trees and isolated shrubs.

MATERIAL AND METHOD

Sterile material

Sterile samples were collected from the ponds of Moldova Noua. There were brought into the laboratory and extracted with a mixture of nitric acid with hydrochloric acid and maintained for 16 hours at room temperature, followed by boiling under reflux for 2 hours. The extract was then cleared and brought to volume with nitric acid. The content

of microelements in the extract was determined by the spectrophotometry method of the atomic absorption.(LAŢO, RADULOV, 2007).

Plant material

The stocktacking of plant species on arranged dumps was appointed for two years using the method developed by Braun-Blanquet (1964), cited by Arsene method (2003). The encountered species were determined by the aid of ''Flora Romaniei'' work (1952-1976). For the determination of heavy metals on spontaneous plants from the ponds, there were selected prevalent plant species from these areas, as follows:

- on the ponds Tăuşani, which is the largest in size (154 ha), was taken for analysis of all four identified plant species: *Salsola kali* species (Russian thistle), a worthless fodder plant, which occupies 60% of the surface of the pond;

- on the ponds Boşneag 1, *Phragmites australis* species occupies about 80% of the total area of the pond, so this plant has been taken under study concerning the content of heavy metals;

-on the ponds Boşneag 2, of a total identified spontaneous species in a significantly higher percentage were discovered species as: *Medicago falcata* (alfalfa), a plant with good fodder value and *Festuca arundinaceea.*

Chemical analysis to determine composition of sample

To determine the content of heavy metals in these plant species, samples were dried and weighed to obtain the extract of which the elements will be determined. It has been weighed 3 g of dried herbs in a 250 ml reaction vessel. It was then moistened with 1 ml of water plus 2 ml of hydrochloric acid while stirring, then 7 ml of nitric acid was added, drop by drop, to avoid foaming. In the absorption vessel were added 15 ml of nitric acid.

The absorption vessel and the refrigerant were attached to the reaction vessel and left 16 hours at room temperature to allow slow oxidation of the organic material of the sterile. After the 16 hours the reaction mixture temperature was raised to reach reflux conditions and maintained for 2 hours, ensuring that the condensation is less than one third of the height of the condenser, then was allowed to cool. Absorption vessel content was added to the reaction vessel, by the refrigerant rinsing the bowl absorption but also the refrigerant in 10 ml of nitric acid. Insoluble residue from the reaction vessel was allowed to settle. Relatively sediment-free supernatant obtained by decantation was carefully passed through a filter paper and the filtrate was collected in 100 ml flask. All the original extract from the reaction vessel was passed through a filter paper, then the insoluble residue on the filter paper was washed with a minimum of nitric acid. Filtrate was then collected with the first.

From the extract thus prepared by the method of atomic absorption spectrophotometry at different wavelengths was determined each item. (LAŢO, RADULOV, 2007).

RESULTS

According to data contained in Table 2, the tailings from Moldova Noua (Caras-Severin) contain a large amount of heavy metals (Cu, Zn, Fe, Pb) in all substrates examined. Values of these elements are very significantly exceeded. Manganese and cadmium content in the tailings, to a depth of up to 40 cm, does not exceed the permissible limit. Copper and zinc had the highest percentage of sterile.

From the literature we found that some plants are known as hyperacumulator plants which accumulate concentrations over 1000 mg / kg heavy metals for Cu (34 species) for Pb (14 species), Cd (one species). Also known concentrations exceeding 10,000 mg/kg for Zn (11 speci) and Mn (10 species). (GHOSH and SINGH, 2005).

The four species of plants (*Salsola kali, Festuca arundinaceea, Medicago falcata and Phragmites australis*) prevailing on the ponds were found to be tolerant plants to heavy metals, due to the fact that they have resisted every year on these so polluted tailings *(table 1*).

Salsola kali, compared with other plant species analyzed, accumulated the largest amount of manganese and zinc in the tailings, and cadmium and lead was not extracted.

Copper was extracted mainly by *Phragmites australis* and *Medicago falcata*.

Tabel 1. Chemical content of plants analyzed

Sample	Mn [ppm]	Cu [ppm]	Zn [ppm]	Fe [ppm]	Cd [ppm]	Pb [ppm]
Salsola kali (thistle)	64	8,7	25	14,7	-	-
Festuca arundinaceea (fescue)	50	7,7	15	19	-	2
Medicago falcata (alfalfa)	50	10	9	15,3	0,01	1
Phragmites australis (reed)	55	13,1	12	16	-	-

Source: MICU (2012)

From the information presented in Table 1, *Medicago falcata* was the only plant species that has accumulated through its roots all six studied heavy metals.

Festuca arundinaceea, the only plant with good fodder value, was identified as predominant in the tailings ponds to extract the greatest amount of lead (2 ppm) and lowest copper (7.7 ppm).

Table 2. The synthesis of experimental results and establish the significance of differences limit values of these metals

Sample	Mn			Cu			Zn			Fe			Cd			Pb		
	Conc. [ppm]	The diffe-rence	Signifi-cance	Conc. [ppm]	The diffe-rence	Signifi-cance	Conc. [ppm]	The diffe-rence	Signifi-cance	Conc. [ppm]	The diffe-rence	Signifi-cance	Conc. [ppm]	The diffe-rence	Signifi-cance	Conc. [ppm]	The diffe-rence	Signifi-cance
V_1 (0 cm)	198.56	- 701.44	000	209.20	189.2	**	230.33	130.33	*	12897.67	12897.67	*	0.15	- 0.85	000	18.00	-2	-
V_2 (10 cm)	141.50	- 758.5	000	337.30	317.3	***	270.25	170.25	*	339.67	339.67	-	0.40	- 0.60	00	78.50	58.5	***
V_3 (20 cm)	49.50	-850.5	000	214.30	194.3	**	369.33	269.33	***	27886.17	27886.17	***	0.46	- 0.54	00	40.70	20.70	-
V_4 (40 cm)	111.48	-788.52	000	344.30	304.3	***	37.40	- 62.6	-	20122.70	20122.70	**	0.00	- 1	000	41.70	21.70	-
Valori limită [ppm]	**900**	witness	-	**20**	witness	-	**100**	witness	-	**0**	witness	-	**1**	witness	-	**20**	witness	-
	$DL_{5\%}$ = 338.83 $DL_{1\%}$ = 456.18 $DL_{0.1\%}$ = 606.59			$DL_{5\%}$ = 127.13 $DL_{1\%}$ = 171.17 $DL_{0.1\%}$ = 227.60			$DL_{5\%}$ = 128.70 $DL_{1\%}$ = 173.28 $DL_{0.1\%}$ = 230.42			$DL_{5\%}$ = 11823.90 $DL_{1\%}$ = 15919.01 $DL_{0.1\%}$ = 21167.68			$DL_{5\%}$ = 0.36 $DL_{1\%}$ = 0.49 $DL_{0.1\%}$ = 0.66			$DL_{5\%}$ = 23.51 $DL_{1\%}$ = 31.66 $DL_{0.1\%}$ = 42.10		

Source: MICU (2011)

CONCLUSIONS

Following the studies on heavy metal accumulation by the spontaneous plants on sterile pounds, we found that the best hyperacumulating heavy metal plant proved to be *Medicago falcata* (alfalfa). Due to its pivoting root, after a few years it reaches depths of 100 cm, exploring a large amount of tailings and also diversified on layers absorbs more elements in larger quantities. Species *Salsola kali, Festuca arundinaceea, Medicago falcata and Phragmites australis* are the most tolerant plants to heavy metals, long resisting on the sterile.

Of the six heavy metals analyzed, manganese was extracted in the largest quantity.

Cadmium and lead cannot be consumed from the sterile by all the plants, only by *Medicago falcata,* and a lead hyperacumulator proved to be *Festuca arundinaceea.* But these two plants with a good forage value will be searched by wild animals (rabbits etc), and birds (pheasants etc) that can transit the ponds and will get poisoned by lead and cadmium. It is one of the causes of herbivores and bird population reduction in these areas.

Although *Salsola kali* is a worthless fodder plant, being a thistle, should be not get away from the land contaminated with heavy metals, being an excellent plant consuming manganese and zinc.

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